University of Pannonia

Chemical Engineering and Material Sciences Doctoral School

Development of organic latent heat storing calcium alginate microcapsules with natural origin

PHD THESIS

Bence László Németh

Chemist

Supervisor:

Dr. Tivadar Feczkó

senior research fellow

2023

Introduction, aims

The renewable heat (solar energy) is available to a high extent in Hungary. The recovery of waste heat of industrial processes and household appliances is still negligibly low. The main reason is that the availability of these energy sources is not synchronised in time and space. The necessary heat quantity must be available in the right time, quantity and temperature level for the industrial, agricultural or household energy use. The temporal heat energy should be stored economically in a recyclable form for a reasonable time period.

A significant part of energy in Hungary is used for heating and cooling of buildings, which will be decreased by minimum 30 % during the next decade according to the "National Energy Strategy 2030". The phase change materials could reduce the heating and air conditioning energy use of buildings by 15-30 % applied in the structural materials, especially with the temporary storage and utilization of temperature fluctuation of environment and the solar energy. This can contribute to a large extent to the exchange of fossil energy sources, thus to the reduction of greenhouse gas emission. Moreover, they decrease the temperature fluctuation substantially, hence improve the comfort feeling of inhabitants qualitatively. The PCMs have been rarely used in Hungary so far, and their research is also scarce compared with international data. Their efficiency and applicability in building structures can be enhanced by microencapsulation. Their widespread use in Hungary can be resolved by competitive and economical Hungarian development and production of microencapsulated PCMs. The potentially available heat storing materials have got unsuitable material and thermal properties: the mostly used organic PCM paraffins are combustible and inflammable. In bulk phase their flammability is high, specific surface for heat transition is small, and the necessary thermal conductivity length is high, which ruins the efficiency of heat transfer and storage. To overcome the problems regarding building industrial application, the microencapsulation and less flammable materials can be used. A significant part of commercially available organic phase change materials is not suitable due to the environmental protecting or life cycle properties, mostly because they are not biodegradable and hence pollute the environment at the end of their lifetime. The commercial capsules are composed of synthetic shell or encapsulating polymers (e.g. phenol-formaldehyde resins, methacrylates), which are disadvantageous in the point of view of environmental protection, and they cannot be deposited after the building demolition. The separation of built-in PCMs from the waste building materials has got especially high energy demand, and it is generally not resolvable, thus has got serious environmental risk. These features inhibit also the global spread of microencapsulated PCMs and their utilization in building structures. The spread in Hungary is further limited by the fact that this type of product is not manufactured in the country at all, because the knowledge and technology to achieve suitable PCM microcapsules are not available in the Hungarian industry. The practical utilization of phase change materials is prohibited, since in building structural elements and in innovative isolating systems which can substitute the traditional isolating materials, their thermal behaviour and widespread applicability have not been investigated thoroughly and in large scale except in some international studies.

The aim of my study was to develop heat storing microcapsules composed of phase change materials and carrier of biological origin and the scale-up of production technology as well as the determination of thermal properties and features of new products. The developed material system should have suitable stability, that is, during its use it must be resistant to environmental effects (temperature fluctuation, mechanical influences, microbial infection). Another requirement is the maximal heat capacity, heat conductivity and heat transfer of microcapsules. The microcapsule material and its properties will have improved quality compared to the known PCM systems. Therefore, the encapsulated and carrier or shell materials were also of natural origin. The microcapsules must have suitable lifecycle features: their quality should be durable (for 20-30 years) in building structural elements; however, after their lifecycle (in case of building demolition, deposition or secondary utilization of waste) they should be quickly degradable without the formation of harmful materials.

Experimental

Paraffin phase change material-calcium alginate core-shell microcapsules were formed by ionic crosslinking/gelation and heat treatment. The process optimisation was done by Statistica software using 3-level 3 factors Box-Behnken experimental design. During microcapsule formation, the effect of three most important process parameters, i.e. sodium alginate and calcium chloride concentrations as well as the contact time of the sodium alginate gelation solution and the core material were investigated on the particle size and paraffin content. By using sodium alginate of high viscosity, the paraffin content of microcapsules was substantially increased; then, the optimised method was used to microencapsulate coconut oil PCM instead of paraffin. The heat storing microcapsules composed of compounds from exclusively biological origin, were functionalised by silver nanoparticles formed by the reduction of silver nitrate using sodium ascorbate reducing agent in order to protect the microparticles from quick bacterial and mould infection.

The particle size and shape were studied by optical microscopy. The yield of microcapsules was determined by gravimetry. The size of silver nanoparticles was measured by dynamic light scattering method using Zetasizer Nano ZS instrument. The morphology of microcapsules was monitored by FEI Apreo scanning electron microscope. FTIR spectra were recorded by Jasco FT/IR-4600 instrument. Thermal analysis of heat storing microcapsules was done by Setaram μDSC3evo differential scanning calorimeter (DSC). The evaluation was achieved by Calistro Processing (v1.12) software. To determine the melting and freezing enthalpies as well as onset and offset temperatures, the baseline integration method was applied. The durability throughout thermal resistance was studied after 1000 heating and cooling cycles by an own designed and built accelerated aging device and repeated DSC analysis. Thermogravimetry was measured by Setaram LabsysEvo instrument in high purity air atmosphere. Silver content was determined by inductively coupled plasma-mass spectrometry (ICP-MS). Silver composition was investigated by X-ray photoelectron spectroscopy (XPS, EA 125 electron spectrometer). The antibacterial efficiency of calcium chloride-coconut oil microcapsules with or without silver nanoparticles was studied on Salmonella serovar Typhimurium SJW2536 species, while antifungal effect was examined on Paecilomyces variotii, Trichoderma viride and Penicillium funiculosum fungi.

New scientific results

1. **:** I developed a repeated interfacial coacervation/crosslinking method to prepare latent heat storing microcapsules with calcium alginate double shell containing paraffin phase change material (PCM). The method is still under patent protection. The influence of most important process parameters was studied by 3-level 3 factors Box-Behnken experimental design and statistical evaluation. I proved that the paraffin content was most substantially influenced by the calcium chloride concentration and the contact time, nevertheless, the sodium alginate concentration was also a key parameter. The calcium alginate-paraffin heat storing capsules had uniform size, core-shell structure, non-porous and double alginate shell and optimally maximum 48 m/m % paraffin content. The prepared microcapsules were leakage free and had good thermal stability and suitable mechanical strength confirmed by thermal analysis and repeated thermal cycling tests. **[S1]**
2. During the preparation of calcium alginate-paraffin microcapsules, the maximal paraffin content of heat storing capsules was increased to 81.5 m/m % by exchanging the sodium alginate of small viscosity (14 mPas) to that of high viscosity (950 mPas) and by optimising the process by Box-Behnken experimental design. I proved that the viscosity of sodium alginate has got of crucial importance regarding the paraffin content, since increasing the viscosity, substantially lower quantity of it was sufficient to emulsify the paraffin. **[S2]**
3. The developed method for paraffin microencapsulation was converted to coconut oil incorporation; hence, I prepared eco-friendly, of fully biological origin and biodegradable heat storing microcapsules. I used a high-viscosity sodium alginate for the capsule formation, which enabled to reach similarly high coconut oil PCM content (81.1 w/w %) to that of paraffin. The high PCM content was reflected in the heat storing capacity measured by both extraction method and differential scanning calorimetry which latter showed 84.7 J/g melting and 84.5 J/g freezing latent heat capacity values. **[S2]**
4. I improved and upscaled the preparation of latent heat storing microcapsules from laboratory to pilot scale. During pilot scale preparation, to prevent the coalescence of PCM cores, I developed a pilot prilling and gelation instrument with air-lift mixing device. To add the core particles to the gelation solution, I developed a pilot dosing

system with Fix-Mix® elements. To scale-up the drying of capsules, I adapted a drying chamber with a conic insert.

5. The shell of calcium alginate-coconut oil PCM microcapsules was functionalised by silver nanoparticles that were formed by the environmentally friendly reduction of silver nitrate. The high coconut oil content of microcapsules was achieved also in the presence of silver nanoparticles confirmed by gravimetry and DSC analysis. The heat storing capability of microcapsules did not change after 200 heating-cooling cycles, which confirmed their appropriate thermal and mechanical stability. The highest silver concentration (1.3 m/m % related to the capsule weight) exerted efficient antimicrobial effect against the studied bacterial and three fungal species. **[S3]**

Publications in the field of PhD thesis

[S1] Németh, B., Németh, Á.S., Tóth, J., Fodor-Kardos, A., Gyenis, J., Feczkó, T. Consolidated microcapsules with double alginate shell containing paraffin for latent heat storage. Solar Energy Materials & Solar Cells, 143 (2015) 397–405. **IF: 4.732, D1**.

[S2] Németh, B., Németh, S.Á., Ujhidy, A., Tóth, J., Trif, L., Gyenis, J., Feczkó, T. Fully bio-originated latent heat storing calcium alginate microcapsules with high coconut oil loading. Solar Energy, 170 (2018) 405-414. **IF: 4.674, Q1**.

[S3] Németh, B., Németh, Á.S., Ujhidy, A., Tóth, J., Trif, L., Jankovics, H., Kriszt, B., Dobolyi, C., May, Z., Gyenis, J., Feczkó, T.: Antimicrobial functionalization of Ca alginate-coconut oil latent heat storing microcapsules by Ag nanoparticles. Int. J. Energy Res. 44 (2020) 11998–12014. **IF: 5.164, Q1**.

Other related publications

[S4] Feczkó, T., Kardos A. F., Németh, B., Trif, L., Gyenis, J. Microencapsulation of n-hexadecane phase change material by ethyl cellulose polymer. Polym. Bull. 71 (2014) 3289-3304. **IF: 1.438, Q2**.

[S5] Feczkó, T., Trif, L., Németh, B., Horak, D. Silica-coated poly(glycidyl methacrylate-ethylene dimethacrylate) beads containing organic phase change materials. Thermochimica Acta, 641 (2016) 24-28. **IF: 2.236, Q2.**

[S6] Németh, B., Ujhidy, A., Tóth, J., Gyenis, J., Feczkó T.: Testing of microencapsulated phase-change heat storage in experimental model houses under winter weather conditions. Build. Environ. 204 (2021) 108119. **IF: 7.093, D1**.

[S7] Németh, B., Ujhidy, A., Tóth, J., Ferencz, M., Kurdi, R., Gyenis, J., Feczkó T. Power consumption of model houses with and without PCM plaster lining using different heating methods. Energy Build. 284 (2023) 112845. **IF: 7.201, D1**.